CHARACTERIZATION OF BIO-OIL & UPGRADATION TO TRANSFORMER OIL

A Thesis submitted for the degree of

Bachelor of Technology

In

Chemical Engineering

By

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CERTIFICATE

This is to certify that the project entitled, "**Characterization of bio-oil &Upgradation to transformer oil**" submitted by **Saroj Kumar Behera**is an authentic work carried out by him under my supervision and guidance for the partial fulfillment of the requirements for the award of **Bachelor of Technology (B. Tech) Degree in Chemical Engineering** at **National Institute of Technology, Rourkela.**

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Abbreviation

1. HC :- Hydrocarbon
2. IFT:-Inter Facial Tension
3. GC-MS:-Gas Chromatography Mass Spectrometry
4. FTIR:- Fourier transform infrared spectroscopy

ABSTRACT

By distillation of crude oil the transformer oil is manufacture. The demand and price increase of crude oil day by day. So we need a renewable source for its generation. Thermal pyrolysis is one of the methodologies which is a renewable technology where waste tire were pyrolysed to obtain fuel oil. It reduces pollution as well as it also cover the daily demand of the energy. In this paper, with in the temperature range of 450^0C to 800^0C, pyrolysis of the waste tire samples were carried out in a semi batch reactor made up of stainless steel. 48.3%was obtained as the optimum output. Physical properties of the oil obtained were determined through using standard test methods and the chemical compositions were analyzed by using GC-MS, FT-IR analyzer. The properties of transformer oil (Properties like PH, viscosity, water content, flash point, pour point) were studied. Then upgradation is made in some properties of tire oil to conclude or prepare the transformer oil.

CHAPTER 1

INTRODUCTION

A bio fuel is a HC that made by or from living organic entity that we human can use as source of energy. Any HC fuel that is delivered from natural matter (once alive material) in brief time (day, week or month) is consider as bio fuel.

By distinctive procedures like natural, thermal and physical methods bio fuel can be changed over in numerous energy forms. Fossil fuels have become limited, and the energy need increase day by day. The increment in the discharges rates of greenhouse gasses released from the utilization of these fossil presents at risk to the world atmosphere. Because of this there is an urgent need to develop alternative energy source which is energies efficient and economical. For production of bio fuel biomass need. Pollution gives a significant motivating force to create bioenergy. The bio fuel produce from bio mass can be a substitute for fossil fuel. Biomass can contribute energy to world for consumption.[1]

Transformer oil produces form crude by distillation. (i.e. solvent extraction, atmospheric or vacuum distillation and dewaxing. After this process by Sulphonation, hydrotreating or hydrogenation the distillate obtained must then be treated.

1.1. Current energy consumption:-

For a developing country energy is an essential requirement. And the requirement is increasing so it need a huge investment

Based on different criteria energy can be classified in different types:-.

A. Commercial energy and Non commercial energy
B. Primary energy and Secondary energy
C. Renewable energy and Non-Renewable energy

1.1.1. Primary energy and secondary energy:-

Primary energy is that form of energy which is available in earth crust. Which can be directly or some process of cleaning it can be utilize for heat production or mechanical work. For example:- coal, petrol, diesel. **Secondary energy** is that which are generate form other form of energy.

1.1.2. Commercial & Noncommercial energy:-

The **commercial energy** is the form of energy which are direct available in market for a definite price. for example:- electricity, petrol etc. and **noncommercial energy** are those which are not available in the commercial market like fire wood, cattle dunk.

1.1.3. Renewable energy and Non-Renewable energy

The energy which are generate from natural resources like wind, water are called as **renewable energy**. Example:- hydroelectricity, geothermal power, wind energy and solar energy. And the non-renewable energy are those which are limited available in nature like fossil fuel and coal.

Today, the world runs on fossil fuels. The main cause for rapid development in 20th century is undoubtedly this mysterious energy treasure, the petroleum.

If we look the present supply of global energy from various sources, still

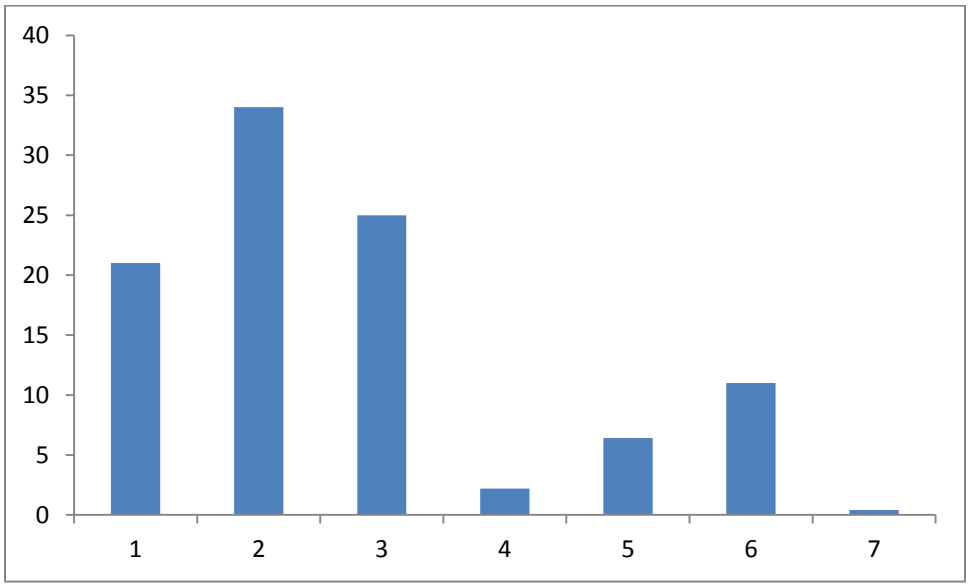

Figure 1.1: Total world energy supply by source

1. Natural gas

2. Oil
3. Coal
4. Nuclear poser
5. Hydropower
6. Bio mass
7. Other

1.2. PROBLEMS WITH FOSSIL FUELS

Fossil energizes as the name recommends are subordinates of plant and creature fossils that are million years of age. These are formed from the remains of the decayed plants and animals of the carboniferous period. The three fuel sources coal, natural gas and oil/petroleum helps to meet the energy and electricity demands of today's world. The three energy sources natural gas, coal and oil/petroleum serve to meet the power and energy demand of today's world. The demand never decreases for the energy.

1.2.1 Disadvantages of Fossil Fuels

1. **Global warming**: Burning of fossil fuel produce carbon dioxide which causes air pollution. It is also a greenhouse gas which is the main cause of global warming.
2. **Rising Prices:** Many country mainly middle west countries have large storage of fossil fuel and for supply of fuel many country depend on them. so the worldwide price of the fossil fuel is increasing.
3. **Acid Rain**: Vehicles & factories all burn fuel and when fuel burn polluted gas produce. Some gas like nitrogen oxide and Sulphur dioxide react with cloud water drop and converted nitric acid and sulpharic acid. Rain from these cloud is cause acid rain.
4. **Non-Renewable :** As the fossil fuels are extracted to an unlimited level it is for sure that they will deplete some day or the other. Since they are non-renewable it is likely that fuels expenses will face a hike in near future. It would take millions of years to replace coal, and oil, and we are using them quickly.
5. **Coal Mining:** Extraction of coal from areas that have huge reserves is not only a difficult and dangerous task but also pose health hazard to the lives of several workers

who work there. The coal mining destroys wide areas of land and results in ecological imbalance.

6. **Need Huge Amount of Reserves :** The coal power plants needs huge and regular supply of coal to produce large amount of electricity on a constant basis. This means they need reserves of coal almost train-loads of fuel near power stations to carry out the process of generating electricity. This is required since today also many nations are dependent on coal as a major source of producing power.

CHAPTER 2

Literature Review

2.1. BIOMASS

Biomass refers to any natural materials that are gotten from plants or living organism. As a rule it is hard to discover the real definition. Biomass is non-fossilized and biodegradable natural material starting from plants, creatures and miniaturized scale organic entities. This incorporates the items, side effects, squanders & deposits from horticulture, ranger service, civil & modern squanders. Biomass likewise incorporates gasses and fluids recuperated from the deterioration of biodegradable natural & non fossilized materials.

2.1.1SOURCES OF BIOMASS

The general sources of biomass are biological,municipal, forest &agricultural.

Theexamples of sources are discussed below.

- Agricultural: food grain, bagasse (crushed sugarcane), seed hulls, corn stalks, nutshells, straw, & manure from cattle, hogs& poultry.
- Forest: trees,bark or wood, sawdust, wood waste, timber slash, & mill scrap.
- Municipal: Sewage sludge, yard clippings, waste paper, &food waste.
- Biological:animal waste&biological waste.

2.2. BIO OIL

Bio oil as it is known from its name is obtained from biological organisms either it may be plants or it may be animals. 80% of the bio oil should be renewable. Literally all types of bio oil are obtained as a product from photosynthesis process so indirectly it can be referred as a source of solar energy. The term bio fuel implies as bio mass fuel(i.e. in the form of solid liquid and gas). Solid bio-fuel includes wood, saw-dust, dried grass-bundles, household twigs and rags, charcoal, agricultural wastage, non-food energy crops and dried manure cakes where biodiesel, bio alcohol, bio-ether, pyrolytic oil are liquid bio-fuel and syn gas and bio gas are gaseous bio-fuel.

2.3. BIOMASS CONVERSION PROCESS:

Biomass is in general converted to useful products mainly by two process:

1. Thermo-chemical process.

2. Bio-chemical processes.

2.3.1 THERMOCHEMICAL PROCESS:

The thermo-chemical process include mainly process like

1. Liquefaction

2. Torrefaction

3. Gasification

4. Combustion

5. Pyrolysis

2.3.1.1 Torrefaction

A moderate heating of biomass in an idle or diminished environment to a maximum temperature of roughly 300°C is Torrefaction. It can likewise be termed as a gathering of products resulting from the halfly controlled & isothermal pyrolysis of biomass occurring for in a temperature scope of 200–280ºC. Subsequently, the methodology can be referred to as a gentle pyrolysis as it happens at the lower temperature scope of the pyrolysis process. Toward the end of the torrefaction procedure, a solid undeviating item with higher vitality content & lower dampness content then crude biomass is obtained. Mostly,other volatiles & the smoke-producing compounds, which creates a finishing up item that will have a higher heating value however a lower mass.

2.3.1.2. Liquefaction

Liquefaction is the procedure of transformation of biomass into bio fuel & chemicals where change over takes place in presence of catalyst & solvent at a temperature of 350^{o}C &pressure of 12-20 MPa.The solvent may be glycerol, phenol & water inhydrogen or nitrogen atmosphere. Alkali maybe adjoined to upgrade organic conversion. Theorganic liquid is the primary product with decreasedoxygen content. The character of these compounds was found to be dependent on the catalyst, butnot perceptible on the physical conditions used.

2.3.1.3. Combustion

Combustion is an exothermic chemical reaction to substantial heat & is a sensation in which the response is naturally proceeded by the heat develop by the response. While utilizing biomass as fuel, the oxidation reaction producing heat, where carbon, oxygen, hydrogen, nitrogen & combustible sulfur contained in biomass respond with oxygen or air, is unquestionably known as ignition, modernly. Burning procedure proceeds by surface response, gas stage response, or both, after procedures, for example, fusion, pyrolysis & evaporation. Thus, in real ignition response, confused phenomena such as evaporation, diffusion, mixture, heat conduction, convection, radiation, and luminescence advance complicated at a very high velocity. As pre mix combustion or diffuse burning, Gas fuel burns straightforwardly in gas phase. As inflammable gas, Liquid fuel burns in gas stage after surface vanishing, which is known as or called as evaporation burning, Heavy oil and so forth burns in evaporation ignition however disintegration burning likewise goes on, where deteriorating the fuel segment happens by the generation of heat.

2.3.1.4. Gasification

Gasification is the change, by halfway oxidation at higher temperature; of carbonaceous feedstock into vaporous fuel. The heating estimation of the yield gasses by and large ranges from about one tenth to 50% of common gas, contingent on the gasification methodology utilized. The

yield gas can be utilized as a part of the era of heat, power through direct terminating in the boiler & motor after clean up. On the other hand the yield gas is habituated to create fuel like hydrogen & methanol forthe energy component. Gasification of biomass has more merits than combustion in the terms of clean & productive operation & financial aspects of scale. In the procedure of gasification the biomass materials goes in exceptional steps. The starting stride of gasification is pyrolysis, where Volatiles are released & carbonaceous molecule heats up & roast is delivered. In the further step ignition procedure happens as some of the char & the unstable items reacts with oxygen to form carbon monoxide & carbon dioxide, which conveys heat for the later gasification responses.

For example: C + ½ O2 -->CO.

In the last stride of gasification happens as the carbon dioxidereacts with char & steam to producehydrogen&carbon monoxide, through the response

C + H2O --> H2 + CO.

2.3.1.5. Pyrolysis:

Pyrolysis is the methodology of heat decay of biomass at normal temperatures without oxygen. The progressions in pyrolysis incorporates: readiness of feedstock & presentation of the food into the reactor, completing the response by assimilation of heat or other expansion of operators, for example, air, steam ,oxygen,, post ignition, hydrogen or handling of the gasses created amid the response step, & fitting direction of the subsequent fluids, ash & char .Pyrolysis item by and large comprises of gasses like CO2, CH4 & NH3 & fluids like bio-oils, ethanol, acetone,acetic acid etc .The relative offset of the yield relies on the procedure & system condition, optimum temperature, attributes of biomass & living arrangement time of material. In this technique the biomass is heat to a temperature go with rapidly cooled & low habitation time to gather the consolidated fluid which is on the other hand known as bio-oil. This is done to keep the deterioration of the transitional items over pyrolysis. At the point when cooled, greatest volatiles gather to from bio-oil. This strategy is an exceptionally main stream process which makes a firm amount of fluid fuel from biomass, which is very parallel to business transportation fills & can be adjusted or moved up to dislodge transportation fuel.High temperatures&Longer home times increment biomass change to gas, & moderate temperatures & short vapor living arrangement

time are ideal for delivering fluids. The most imperative character for pyrolysis to jump out at give fitting bio oil yield is:

1. Vapor living arrangement times of about under 2 sec to decrease the Secondary reaction responses to happen.
2. The remaining bio-Char must be Removed to keep the Secondary cracking reaction.
3. The vapors are quickly cooled to deliver the bio oil as the halfway item.
4. In request to get bio oil in greatest, a Temperature of around (400-5000C).
5. With about under 3mm size of finely ground biomass with high heating.

2.3.2. BIO-CHEMICAL PROCESS:

This procedure includes product included for biochemical change of the biomass like bio waste bio waste & bio waste. Now and then it additionally manages paper plant deposits & vitality crops. It joins strategies like enzymatic activity, hydrolysis & pretreatment.

Alternate sorts of biochemical methodology include alcoholic maturation & anaerobic absorption process. The previous methodology includes the deterioration of the natural material in vicinity of organisms without oxygen to create the alleged biogas which embodies carbon dioxide & methane as the real parts. From fertilizer of bovine biogas is for the most part creates, It is utilized as a part of creating power due to higher calorific quality .then again the alcoholic aging procedure includes the generation of wines from the biomass like sugar harvests & starch crops. It includes the activity of life forms like yeast that aides in yield of amazing fuel for transportation reason .For this procedure at first the mixes expected to be separated by hydrolysis as it contains longer chains of Polysaccharide. In the creation procedure of ethanol, It can be refined & can be utilized as fuel as petrol.

2.4. Upgrading of Bio Oil

The injurious properties of high consistency, high oxygen content, warm flimsiness & destructiveness present numerous deterrents to the substitution of fossil determined energizes by bio-oils. In this way, bio-oils ought to be overhauled utilizing legitimate strategies before they can be utilized as a part of diesel or gas motors. Bio-oil can be redesigned physically, artificially & synergistically.

2.4.1. Physical Up gradation of bio-oil

The most critical influencing factor of bio-oil fuel quality are contrarily with convention powers from the high oxygen substance of the bio-oil, high solids content, high consistency, & synthetic unsteadiness.

2.4.1.1.Filtration

Hot-vapor filtration could decrease the amount of ash content of the oil to under 0.01% and the alkali content to under 10 ppm, much lower than reported for biomass oils produced in systems using only cyclones seperators. This gives a higher quality item with lower burn, however scorch is reactantly dynamic & possibly breaks the vapors, lessens yield by up to 20%, decreases consistency & brings down the normal sub-atomic weight of the fluid item. There is restricted data accessible on the execution or operation of hot vapor channels, yet they can be indicated & perform like hot gas channels in gasification forms.

Diesel motor tests performed on unrefined & on hot-separated oil demonstrated a generous increment in blazing rate & a lower ignition delay for the last, because of the lower normal atomic weight for the sifted oil. Hot gas filtration has not yet been shown over a long haul process-operation. Fluid filtrationtolow molecule sizes of beneath around 5 mm is exceptionally troublesome because of the physic-substance nature of the fluid & more often than not requires high weight drops &self cleaningchannels .

2.4.1.2. Dissolvable expansion

Polar solvents have been utilized for a long time to homogenize & diminish the thickness of biomass oils. The expansion of solvents, particularly methanol, demonstrated a critical impact on the oil strength. Diebold &Czernik found that the rate of thickness expand ("maturing") for the oil with 10 wt.% of methanol was very nearly twenty times not exactly for the oil without added substances.

2.4.1.3.Emulsions

Pyrolysis oils are not miscible with hydrocarbon energizes but rather they can be emulsified with diesel oil with the guide of surfactants. A procedure for creating stable smaller scale emulsions with 5-30% of bio-oil in diesel has been produced at CANMET. The University of Florence, Italy, has been dealing with emulsions of 5-95% bio-oil in diesel to make either a vehicle fuel or a fuel for force era in motors that does not oblige motor adjustment to double fuel operation. There is limited experience of utilizing such fuels as a part of motors or burners, however fundamentally larger amounts of erosion, corrosion and disintegration were seen in motor applications contrasted with bio-oil or diesel alone. A further downside of this methodology is the expense of surfactants & the high vitality needed for emulsification.

2.4.1.4.Water content:-

Separator type	Water type removed		
	Free	Emulsified	Dissolved
Gravity	Yes	Some	No
Centrifuge	Yes	Some	No
Coalescing	Yes	Some	No
Absorbent polymer	Yes	Yes	No
Vacuum distillation	Yes	Yes	Yes
Headspace dehumidification	Yes	Yes	Yes

Table 2.1: Water removal technique

Centrifuge: - By turning the liquid, the distinction in particular gravity between the liquid & the water is amplified. Outward separators evacuate free water speedier than gravity separators. They likewise uproot some emulsified water relying on the relative quality of the emulsion versus the diffusive power of the separator. Outward separators don't uproot broke down water. They are a phenomenal alternative for persistent purification of liquids with great demulsibility (water differentiating qualities).

Absorbent polymer separation free:-Emulsified water is gathered by super spongy polymers impregnated in the media of specific channels. These look like traditional turn on or cartridge sort channels. The water causes the polymer to swell & stay caught in the channel's media. Superabsorbent channels can uproot just a constrained volume of water before creating the channel to go into weight drop prompted detour. They are not appropriate for uprooting vast volumes of water, yet they are an advantageous approach to keep up dry conditions in frameworks that don't regularly ingest a great deal of water. These channels don't uproot broke up water.

Vacuum Distillation:-This method successfully removed free, emulsified &dissolved up water. Vacuum refining units work by conveying oil over a vast surface range & adequately heating up the water by expanding the temperature to more or less 150°F to 160°F (66°C to 71°C) & making a vacuum of around 28 inches Hg. At 25 inches Hg, water bubbles at roughly 133°F (56°C). These gadgets viably evacuate water at a temperature that does not bring about much harm to the base oil or added substances. Vacuum refining will likewise uproot other high vapor weight contaminants like refrigerants, solvents & fills. There is some danger of added substance vaporization with this procedure.

Headspace Dehumidification:-These units work by expelling air from the headspace of a sump, dehumidifying it then sending an equivalent volume (or a helped volume, sometimes) of air back to the store to look after weight. On the chance that the oil contains water defilement, it will relocate to the dry air, which is inevitably sent to the dehumidifier for evacuation. The

considerable focal point of this procedure is that it never contacts the oil. This procedure will evacuate free, emulsified & disintegrated 2.4.2. Catalytic upgrading of bio-oil

2.4.2.1. Natural ash in biomass

Before considering catalytic upgrading of bio-oil, it is importantto appreciate firstly that biomass contains very activecatalysts within its structure. These are the alkali metals thatform ash & which are essential for nutrient transfer &growth of the biomass. The most active is potassiumfollowed by sodium. This act by causing secondary cracking ofvapours& reducing liquid yield & liquid quality, &depending on the concentration the effect can be more severethan char cracking.

Ash can be managed to some extent by selection of crops& harvesting time but it cannot be eliminated from growingbiomass. Ash can be reduced by washing in water or diluteacid & the more extreme the conditions in temperature orconcentration respectively, the more complete the ashremoval. However as washing conditions become moreextreme firstly hemicellulose & then cellulose is lostthrough hydrolysis. This reduces liquid yield & quality. Inaddition, washed biomass needs to have any acid removed ascompletely as possible & recovered or disposed of & thewet biomass has to be dried.

So washing is not often considered a viable possibility,unless there are some unusual circumstances such asremoval of contaminants. Another consequence of high ashremoval is the increased production of levoglucosan whichcan reach levels in bio-oil where recovery becomes an interestingproposition, although commercially markets need to beidentified and/or developed.

2.4.2.2. Upgrading to bio oil

Upgrading bio-oil to a conventional transport fuel such asdiesel, gasoline, kerosene, methane & LPG requires fulldeoxygenation & conventional refining, which can beaccomplished either by integrated catalytic pyrolysis as discussedabove or by decoupled operation as summarized below. There is also interest in partialupgrading to a product that is compatible with refinerystreams in order to take advantage of the economy of scale& experience in a conventional refinery.

Integration intorefineries by upgrading through cracking &/or hydrotreatinghas been reviewed by Huber &Corma.

-Hydrotreating

- Catalytic vapour cracking

-Esterification & related processes

-Gasification to syngas followed by synthesis to hydrocarbonsor alcohols.

2.5. Transformer oil

Transformer oil or insulating oil is a high-refined naturally occurring mineral oil that is stable (non reacting) at high temperatures and has terrific electrical insulating or non conducting properties. It is used in oil-operated transformers, some of this are high voltage capacitors, fluorescent lamp ballasts, and some types of high voltage switches and circuit breakers. Its functions are to stop conduction and to act as an coolant.

The oil not only helps in cooling down the transformer but also provides part of the electrical insulation between internal live parts. Transformer oil should remain stable at extreme temperatures for a long period. To increase the cooling, large Power-transformers are fitted with oil filled up tanks with external radiators which cools down by natural convection process. Very large or high-power transformers (with capacities of thousands of kVA) may also have cooling fans, oil pumps, & even oil-to-water heat exchangers.

Large, high voltage transformers undergo prolonged drying processes, using electrical self-heating, the application of vacuum, or both to ensure that the transformer is completely free of water vapor before the cooling oil is introduced. This helps prevent corona formation & subsequent electrical breakdown under load.

Oil filled transformers with a conservator may have a gas finder hand-off (Buchholz hand-off). These security gadgets recognize the development of gas inside the transformer because of crown release, overheating, or an inner electric curve. On a moderate amassing of gas, or fast weight rise, these gadgets can trip a defensive electrical switch to expel power from the

transformer. Transformers without conservators are typically furnished with sudden weight transfers, which perform a comparative capacity as the Buchholz hand-off.

The flash point minimum140 °C & pour point maximum−6 °C are respectively.

Large transformers for indoor use must either be of the dry type, that is, containing no liquid, or use a less-flammable liquid.

Generally there are two types of transformer Oil used in transformer:-

- Paraffin based transformer oil
- Naphtha based transformer oil

The parameters of transformer oil are categorized as,

1. **Electrical parameters**:–

   Specific resistance,dielectric strength, dielectric dissipation factor.

2. **Chemical parameter**:-Acidity,water content, sludge content.
3. **Physical parameters** - Inter facial tension, viscosity, flash point, pour point.

Electrical parameters

- 90°C is 35 × 1012 ohm–cm & at 27°C it is 1500 × 1012 ohm–cm was minimum standard specific resistance of transformer oil at.

Chemical parameters

- **Water content** in oil is allowed up to 50 ppm as recommended by IS-335(1993).
- The accurate measurement of water content at such low levels requires very sophisticated instrument like Coulometric Karl Fisher Titrator.
- **Acidity** of transformer oil is destructive property. On the chance that oil gets to be acidic, Water content in the oil gets to be more solvable to the oil. Acidity quickens the oxidation transform in the oil. Corrosive additionally incorporates rusting of iron.

Physical Parameters

- **Flash point**Flash point is essential that it indicates the possibilities of flame danger in the transformer. So it is have high flash point.(it is more than 140oC).
- **Pour point** of transformer oil is an essential property predominantly at the spot where atmosphere condition is cool. In the event that the oil temperature fall below the pour point, transformer oil stop convection flowing & discourage cooling in transformer. As paraffin based oil has more wax content.it has higher estimation of pour point.
- Oil ought to have **low viscosity** so it can offer less imperviousness to the convectional flow of oil there by not influencing the cooling of transformer. Low viscosity of transformer oil is vital, yet it similarly critical that, the viscosity of the oil ought to increment as less as would be prudent with lessening in temperature.

CHAPTER 3

MATERIALS AND METHODS

3.1 Raw material :-

The raw material use for production of oil was old tire of bicycle collected from nearby cycle repair store. These are cut into approximate 1 cm size and remove the thread.The transformer oil was directly purchased form market.

Proximate and ultimate analysis of raw material:-

By ASTM D3173-75 the proximate analysis was done. And by using Elemental CHNS analyzer the ultimate analysis was done. The samples such as tyre were identified with the following characteristics using proximate and ultimate analysis. Table 3.1 from this table we have rough idea about volatile matter and the fixed carbon content. From Proximate analysis tyre shows less moisture content and more volatile matter content.

Proximate analysis	
Moisture content	0.53
volatile matter	61.25
Ash content	19.44
Fixed carbon (By diff.)	18.78
Ultimate analysis	
Carbon	57.38
Hydrogen	5.50
Nitrogen	0.67
Sulphur	3.24
Oxygen	33.21
H/C Molar ratio	0.10
C/N Molar ratio	86.26
Empirical formula	$C_1H_{1.15}N_{0.01}S_{0.02}\ O_{0.43}$

Table 3.1 Proximate and Ultimate analysis of Tyre sample

3.2 Semi-Batch Pyrolysis Reactor:-

The reactor was made of stainless steel (SS).

- Dimensions:-

  Length:- 16 cm

  Diameter:- 5 cm (Outer)

  4.8 cm (Inner)

One end was sealed & other ends have two outlet. (One for outlet of oil & other for nitrogen purging).

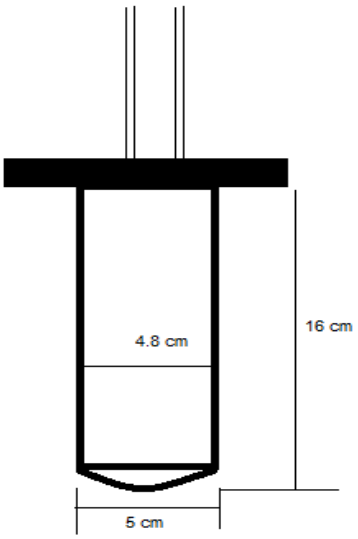

Figure 3.1: Diagram of Batch reactor

3.3 Pyrolysis setup:-

The pyrolysis setup was consisting of batch reactor and furnace (which was shown in fig. 3.2). The furnace was control by PDI controller. Two 500 ml condenser in series was attached to one outlet for condense the vapours coming out of it and other outlet for nitrogen purging. At the end of condenser place a flash for collection of oil.

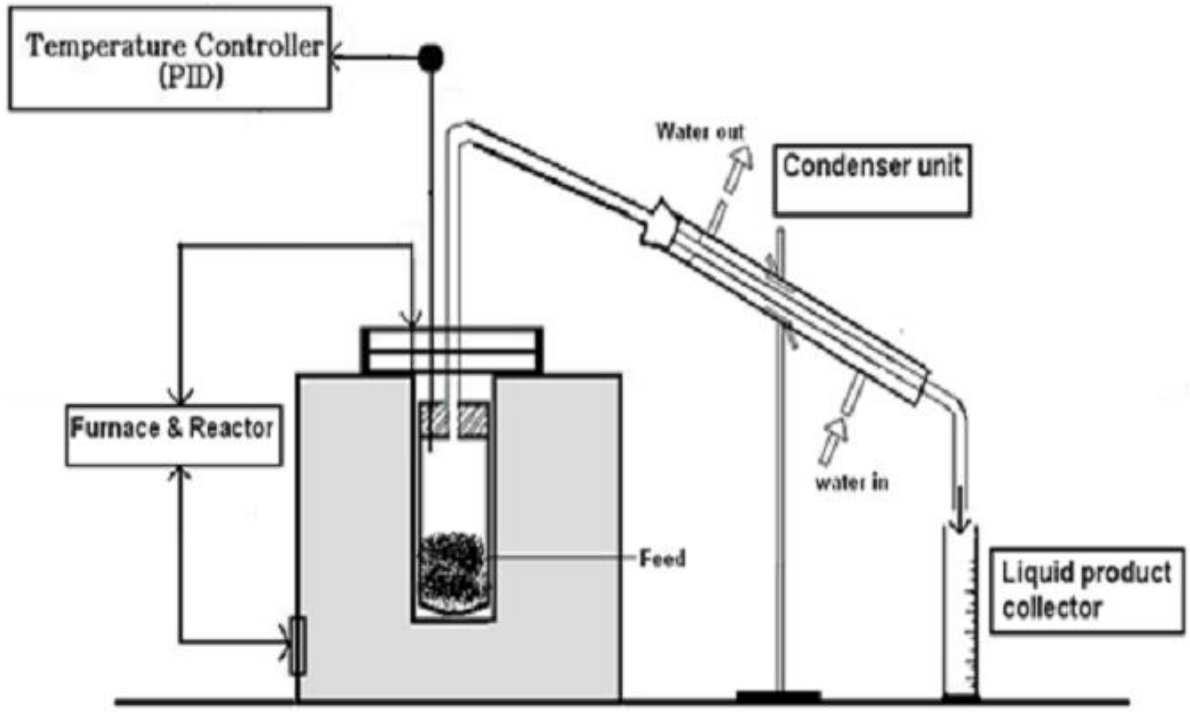

Figure 3.2: Schematic diagram for thermal pyrolysis setup

3.4 Experimental procedure:-

For each run 30 grams of sample was taken in batch reactor. Then it placed in the furnace. At rate of 20^0C/min pyrolysis is carried out at various temperatures (350 ^{0}C to 800 ^{0}C). The condensable liquids are collected in the flask. The non-condensable vapours are vent to the open atmosphere. After the setup cooled down the sample taken in reactor are collected and measure there weight. Then non-condensable vapours weight was calculated by mass balance.

3.5 Characterization of pyrolytic oil:-

3.5.1 Chemical characteristics of tyre oil

3.5.1.1 Fourier Transform Infrared spectroscopy (FTIR)

Using Fourier Transform Infrared spectroscopy (FT-IR) the oil was analysis. In the range of 400-4000 cm-1 region with 8cm-1 resolution ihe FTIR spectra were collected.

3.5.1.2 GC-MS analysis:-

By GC–MS analyzer the chemical composition of tyre-oil was examined with a quadruple detector and a DB1MS capillary column (30 mm × 0.25 mm inner diameter × 0.25 μm thickness). Helium was used as the carrier gas with a constant flow of 1.2 mL/min. The initial temperature of oven temperature program was set at 40°C and continued for 4min, rising by 5°C/min to 250°C, which continued for 10 min. The injector temperature was 250°C.The volume of injected sample (10% of bio-oil in chloroform) was 1 μL. Electron ionization (EI) was used in the MS and standard mass spectra with 70 eV ionization energy were recorded with a scanned range from 0 to 1200 amu.

3.5.1.3 CH-NS analysis:-

Carbon, Hydrogen, Nitrogen, Sulphur content of bio oil and transformer oil was determined. In the combustion process (furnace at ca. 1000 ^{0}C), carbon is converted to carbon dioxide; hydrogen to water; nitrogen to nitrogen gas/ oxides of nitrogen and sulphur to sulphur dioxide. If other elements such as chlorine are present, they will also be converted to combustion products, such as hydrogen chloride. A variety of absorbents are used to remove these additional combustion products as well as some of the principal elements, sulphur for example, if no determination of these additional elements is required.

The combustion products are swept out of the combustion chamber by inert carrier gas such as helium and passed over heated (about 600o C) high purity copper. This copper can be situated at the base of the combustion chamber or in a separate furnace. The function of this copper is to remove any oxygen not consumed in the initial combustion and to convert any oxides of nitrogen to nitrogen gas. The gases are then passed through the absorbent traps in order to leave only carbon dioxide, water, nitrogen and sulphur dioxide.

3.5.2 Physical characteristics of tyre oil

Physical properties such as specific gravity, density, Kinematic viscosity, flash point, fire point, pour point, cloud point, sulphur content and distillation boiling range of the tyre oil was determined using the following standard methods.

3.6 Blending properties

Blending of tyre oil with methanol and transformer oil was carried out in different concentration(10 %wt, 20 %wt,30 %wt, 40 %wt, 50 %wt) and different properties are measure and the graph was plotted between concentration of methanol and transformer oil vs the properties(like viscosity and engine perfomance).

3.6 Upgradation

3.6.2 Water Content

3.6.2.1 Gravity Separation: As water generally comprises of higher specific gravity than the hydraulic fluid, water with tendency to settle at the bottom of the reservoir, given enough resident time in a static environment. With increase in the fluid's temperature & employing a cone shaped differianting tank improves the effectiveness of gravity separation. Polar additives, oxidation byproducts & high fluid viscosity & impurities depicts the effective separation of water & oil. Gravity separation alone does not distance dissolved water or tightly emulsified.

3.6.2.2 Centrifugal Separation:- Spinning of the fluid makes the difference in specific gravity between the fluid & the water is stretched. Free water is removes more faster in centrifugal separators than gravity separators. Removing of some emulsified water depending upon the centrifugal force of the separator vs. the relative strength of the emulsion. Dissolved water is not removed by Centrifugal separators. They are an excellent option for continuous decontamination of fluids with excellent de emulsibility (water separating characteristics).

3.6.3 pH:

The tire oil pH was found to be 4 using pH paper. By blending of KOH with tire oil we have checked the pH of the oil & maintained it to a range of 6-7.

CHAPTER 4

RESULTS & DISCUSSION

4.1 Thermal pyrolysis result:-

In the temperature range of 450 to 700 the product are obtain. The yield % are noted for every elevation of 50^0C for the feed size 1cm which shown in table 4.1. the temperature, weight % of oil, char and volatile matter were plotted together in figure 4.1. At 500 to 550 ^{0}C the tyre was partially pyrolysed. It produce less oil and volatile matter. Retention of char is maximum at this range. Further increase in temperature, more gas is produce observed at 550°C to 600°C along with high oil products, which increases up to 650°C and that explains the effect of temperature on product yield. It was also proved that oil yield increases from 21.64% to 48.3 % by weight at 450°C to 600°C, there after no significant change occurs. It can be postulated that the optimum yield of oil was obtained at 600°C temperature, due to the strong cracking of tyre rubber and the secondary cracking which takes place inside the reactor, and that was followed by formation of more gases, with a significant decrease in residue from 71.3 % to 41.6% by weight for temperature increase from 450°C to 700°C.With increase in reaction time, results that incomplete depolymerisation of the sample that leads to production of more char and less amount of oil at low temperature. The decrease in reaction times contributes to secondary reaction of the products with higher temperature, which leads to more oil and less char. There is no obvious mechanism for gas loss with reaction time.

Table 4.1: Product distribution of tyre pyrolysis

Temperature(^{0}C)	Oil(wt%)	Reaction time(Sec)	Char(wt%)	Volatile matter(wt%)
450	21.6	60	71.3	7.1
500	38.7	54	48.8	12.5
550	42.3	42	46.6	11.1
600	45.8	41	42.3	11.9
650	48.3	37	42.8	8.9
700	47.9	34	41.6	10.5

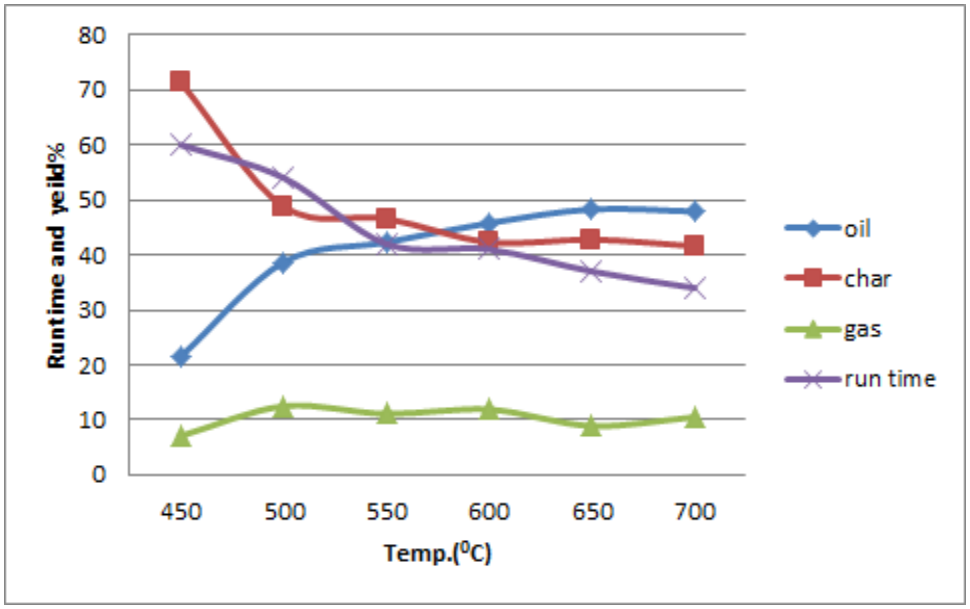

Figure 4.1: Effect of temperature on product yield and reaction time of tyre pyrolysis

4.2 Physical properties:-

After oil obtain the physical properties analyses. The pyroliyic tire oil was dark brown in color. The physical properties are tabulated in table 4.2.

Table 4.2 Physical properties of tyre oil and Transformer oil

Properties	**Tyre oil**	**Transformer oil**
Density(kg/m$^{3)}$	915.3	893.6
Kinematic viscosity	4.19	12.25
Flash point(^{0}C)	50	140
Fire point(^{0}C)	59	305
Pour point(^{0}C)	19	-6
Cloud point(^{0}C)	22	-3
Colour	Dark brown	Transparent brown rad

4.3 Chemical properties of the pyrolytic oil:-

4.3.1 CHNS analysis of tyre oil:-

CHNS analysis of tyre oil and transformer oil was done and the result are shown in table 4.3.

Table 4.3: CH-NS Analysis result

Element	Tyre oil	Transformer oil
C	57.12	39.58
H	7.31	5.744
N	0.59	3.249
S	3.01	2.993
O	31.97	48.476
Empirical formula	$C_{100}H_{143}NS_2\ O_{44.9}$	$C_{14}\ H_{24.2}NS_{0.34}O_{13}$

4.3.2 FT-IR analysis of tyre oil:-

Fourier Transform Infrared (FT-IR) Spectroscopy is one of the imperative strategies which construct its usefulness with respect to the rule that all particles observed infrared light. Just the monatomic (He, Ne, Ar, and so forth) and homopolar diatomic (H2, N2, O2, and so on) particles don't obesrved infrared light. On connection of an infrared light with oil, synthetic bond will extend, contract, and retain infrared radiation in a particular wave length go in any case structure of whatever remains of the atoms. In view of this rule useful gathering present in the tire oils were recognized. The FT-IR range for tire oils is demonstrated in Fig 4.2 outcomes from the transmittance ranges are introduced in Table 4.4. The information demonstrates that the present oils contain basically aliphatic and aromatic

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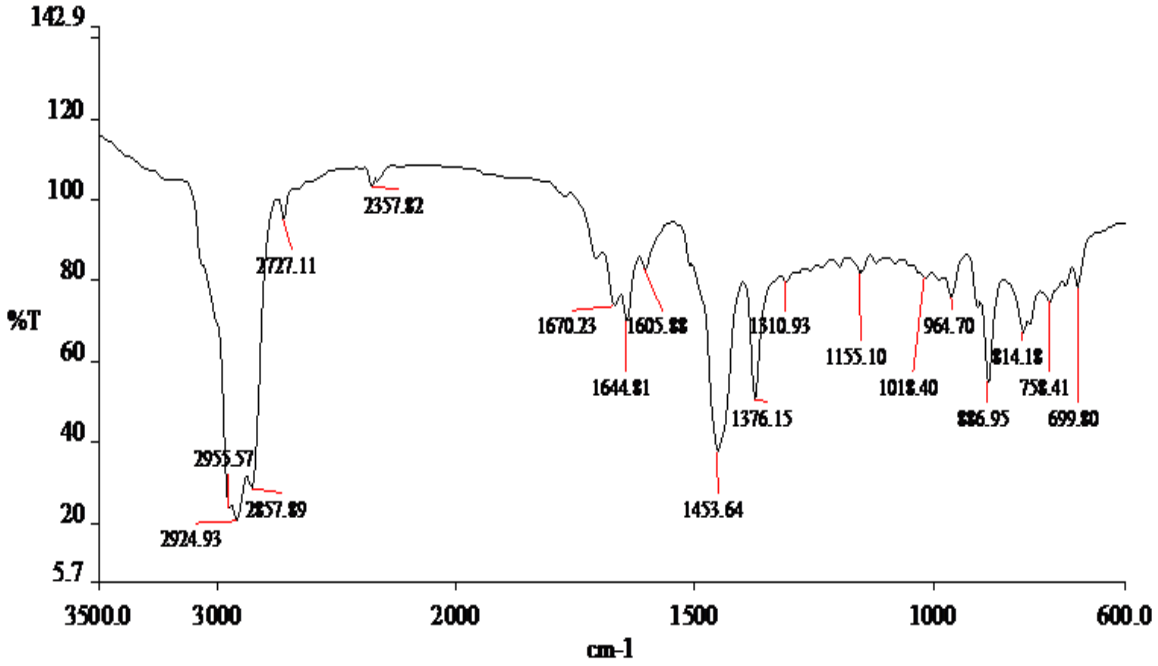

Figuer 5: FT-IR spectra of tyre pyrolytic oil

Wavelength Range (Cm^{-1})	Functional group	Class of compounds
814.18	C-H bending	Alkene+ Phenyl ring substitution
886.95	C-H bending	Alkene
964.70	C-H bending	Alkene
1310.93	C-N stretching	Amines
1376.15	C-H bending	Alkane
1453.64	C-H bending	Alkane
1605.88	C-C stretching	Aromatic compounds
1644.81	C=C stretching	Alkane+ N-H Bend
1670.23	C=O stretching	Aldehyde or ketones
2727.11	C-H stretching	Aldehyde
2955.67	C-H stretching	Alkene

Table 4.4: FT-IR functional groups of tyre pyrolytic oil

4.3.3 GC-MS Analysis of tyre oil:-

GCMS is the one methodology by which we ca found out the organic compound in a sample. The tyre oil obtain form 650^0C pyrolysis process was analysis by this technique and it found that there are 68 compound of different HC. Which are mansion in table 4.5.

Table 4.5: Result of GC-MS analysis:-

Sl.no.	Area	Run time	Name
1	0.57	6.038	Bicyclo[3.1.0]hexane, 1,5-dimethyl-
2	0.84	6.476	2-Ethyl-3-methylcyclopentene
3	1.68	7.263	Phenylethane
4	2.08	7.553	Benzene, 1,4-dimethyl-
5	1.01	7.991	4-Methyl-1-cyclohexene
6	1.30	8.303	1,4-Xylene
7	0.67	8.653	1-methylcyclohexene-5-carboxaldehyde
8	0.79	8.905	1-epoxy-2-methyl-3-isobutenyl-1,4-pentadiene
9	1.66	9.440	Benzene, 1,2,3-trimethyl-
10	0.49	9.834	p-Menth-1-ene
11	1.26	10.168	1,3,6-Heptatriene, 2,5,6-trimethyl-
12	3.92	10.799	Benzene, 1-ethyl-4-methyl-
13	1.46	11.082	1,3-Cyclopentadiene, 5,5-dimethyl-1-propyl
14	2.02	11.498	(4E,6Z)-2,6-Dimethyl-2,4,6-octatriene
15	2.11	11.839	Benzene, 1,2,3-trimethyl
16	1.97	12.196	2,3,6-Trimethyl-1,5-heptadiene
17	9.47	13.199	l-Limonene
18	1.93	13.830	m-Propyltoluene
19	2.93	14.662	beta.-Cymene
20	0.77	15.375	3-(p-Methylphenyl)propanal
21	1.35	15.628	Benzene, tert-pentyl
22	0.59	16.200	Tricyclo[2.2.1.0(2,6)]heptan-3-ol, 4,5,5-trimethyl
23	0.74	16.490	1H-Indene, 2,3-dihydro-4-methyl-
24	2.27	16.839	1-Phenyl-1-butene

25	1.92	17.990	Benzene, (3-methyl-2-butenyl)-
26	1.19	18.317	1H-Indene, 2,3-dihydro-4,7-dimethyl-
27	0.54	18.674	2-Cyclopentene-1-acetaldehyde, 2-formyl-.alpha.,3-dimethyl-
28	1.12	19.053	1-Thia-2-azaindene
29	3.61	20.078	Naphthalene, 1,2-dihydro-6-methyl-
30	1.82	20.687	Naphthalene, 1-ethyl-1,2,3,4-tetrahydro
31	2.09	21.073	Naphthalene, 2-methyl-
32	2.39	21.980	1H-Indene, 2,3-dihydro-1,1,4-trimethyl-
33	2.32	22.448	1H-Indene, 2,3-dihydro-1,1,3-trimethyl-
34	0.80	22.990	Benzene, (3,3-diethoxy-1-propynyl)-
35	2.89	23.265	1,2,3-Trimethylindene
36	0.94	23.733	6,8-Nonadien-2-one, 6-methyl-5-(1-methylethylidene)
37	2.04	24.045	Naphthalene, 2,7-dimethyl-
38	3.59	24.528	Naphthalene, 2,6-dimethyl-
39	2.51	25.077	2-Pyrimidinamine, 5-chloro-4,6-dimethyl
40	4.36	25.575	Naphthalene, 1,2,3,4,4a,5,6,8a-octahydro-4a,8-dimethyl-2-(1-methylethenyl)-, [2R
41	2.74	26.585	2,7-Naphthalenediol, decahydro-
42	1.44	27.254	Naphthalene, 2,3,5-trimethyl
43	0.80	27.655	Naphthalene, 1,6,7-trimethyl
44	0.79	27.997	EUDESMA-3,11-DIENE
45	1.95	28.814	o-Methylbiphenyl
46	0.88	29.334	2-(4-Methylphenyl)pyridine
47	0.71	29.973	Pyridine, 4-(phenylmethyl)-
48	0.45	30.589	Naphthalene, 1,6-dimethyl-4-(1-methylethyl)
49	0.87	31.057	n-Heptadecane
50	1.17	31.481	1,4,5,8-Tetramethylnaphthalene
51	0.47	32.030	Benzene, 1,2-dimethyl-4-(phenylmethyl)-
52	0.56	32.417	Benzofuranone, 3,3-dimethyl-
53	0.32	32.907	3,3',7,7'-Tetramethyl-1,1'-bi(tricyclo[3.3.0.0(3,7]octyl

54	0.25	33.204	n-Hexadecane
55	0.90	33.761	Cembrene
56	0.76	34.155	Fluorene, 4-[1,2-dihydroxyethyl]-
57	0.48	34.616	(all E)-9,13-bis(Demethyl)retinal
58	0.48	34.987	2-Phenyl-4-tertiobutylpyridine
59	0.69	35.359	Hexadecanenitrile
60	0.86	35.678	Isocyclocitral
61	0.52	37.899	2,10-Dimethylethylanthracene
62	1.39	39.273	Heptadecanenitrile
63	0.64	40.165	[4,4'-Bipyrimidine]-2,2',6(1H,1'H,3H)-trione, 5-methyl
64	0.28	41.197	BETA.-ACETOXYDIHYDRODRIMENIN
65	0.38	42.542	2,2,6-Trimethyl-1-(2-methyl-cyclobut-2-enyl)-hepta-4,6-dien-3-one
66	0.74	41.695	3R,4R,5R)-5-Acetoxycaryophyll-8(13)-ene-3,4-epoxide
67	0.26	43.069	2,3-Dihydro-7-methyl-5-phenyl-1H-1,4-benzodiazepine-2-thione
68	0.25	43.441	Benzoimidazol-2-one, 1-adamantan-1-yl-1,3-dihydro

4.4. Upgradation of tire oil:-

4.5. Blending properties:-

Blending of tyre oil with methanol was carried out in different concentration(5 %wt, 10 %wt,15 %wt) and result are show in Table 4.6.

Viscosity:-

Ratio	Weight % of methanol	Time (sec)	Kinematic Viscosity(mm^2/sec)
1:19	5	198	3.94
1:9	10	180	3.58
3:17	15	156	3.1
100:0	100	36	0.7164

Table 4.6: Viscosity of blending of oil with methanol

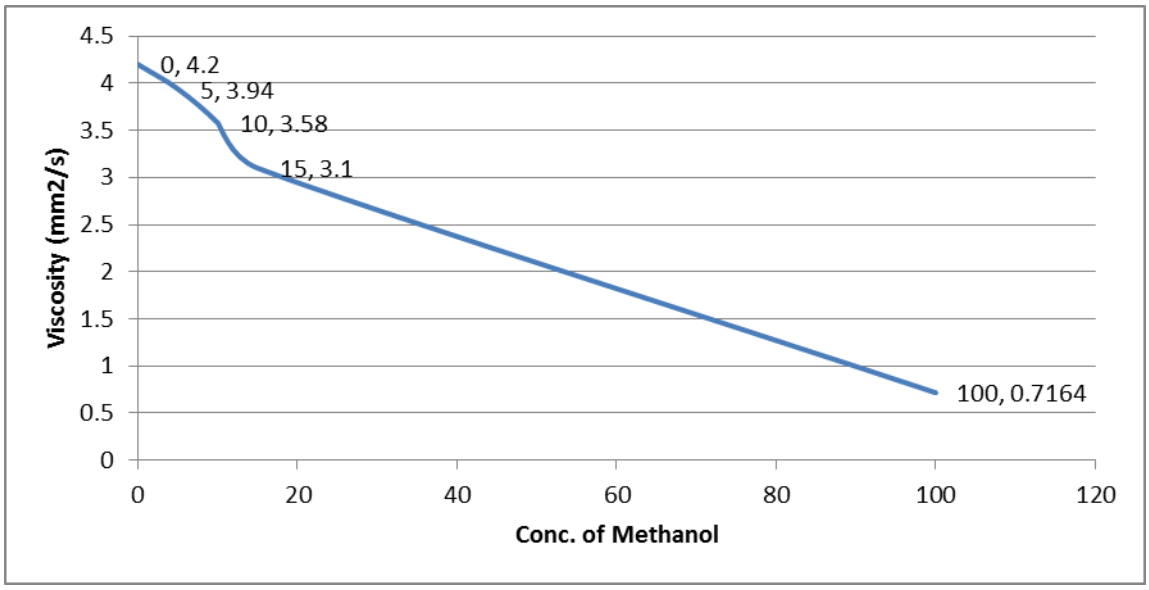

Figure 6 : Concentration Of Methanol vs Viscosity

4.5.1. Water content:-

Water content by gravity separation is negligible & reduction by centrifuge is 3.6 %wt.

4.5.2. pH:-

pH of the tire oil can be maintained by adding KOH and tested by pH paper.

CHAPTER 5

CONCLUSION & FUTURE WORK

5.1 CONCLUSION

In this research thermal pyrolysis of tire oil has been studied. The pyrolysis is done in different temperature (in the range of 450^{o}C to 700^{o}C) and the following observation were observer:-

- The maximum yield obtaines 48.2% at a optimum temperature of 650^{o}C.
- It is conclude from GC-MS and FTIR analysis that the chemical composition of the tyre pyrolytic oil is mainly aromatic and aliphatic compound. From GC-MS analysis we found that oil content 68 compounds of varying carbon chain.
- Viscosity of the oil change was studied when blended with methanol and transformer oiland graph was ploted.
- Maintain the water content, viscosity, flash point, PH, pour point and other properties we can upgrade the tyre oil to transformer oil.

5.2 Future work

- There may be better process by which we can produce tyre oil with more efficent product.
- Use of different catalyst may produce high yield.
- The oil can reduce the fuel demad.

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